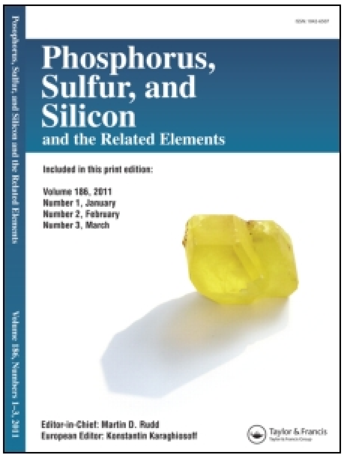

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Triphenylphosphine-Catalyzed Nucleophilic α-Addition to Alkyl Propiolates Synthesis of α-Substituted Alkyl Acrylates

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TRIPHENYLPHOSPHINE-CATALYZED NUCLEOPHILIC α-ADDITION TO ALKYL PROPIOLATES SYNTHESIS OF α-SUBSTITUTED ALKYL ACRYLATES

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The α-addition of NH-acids such as pyrrole, indole, imidazole, or benzimidazole to methyl or ethyl propiolate proceeds under neutral conditions in the presence of a catalytic amount of triphenylphosphine to give the corresponding α-substituted alkyl acrylates.

Keywords: Alkyl acrylates; alkyl propiolates; NH-acids; nitrogen heterocycles; triphenylphosphine

Organophosphorus compounds have been extensively used in organic synthesis as useful reagents as well as ligands of a number of transition metal catalysts.[1–4] However, there are few reactions in which organophosphorous (III) species work as catalysts.[5,6] The phosphine-induced isomerization of alkynoates to 2,4-dienoates[7] and addition of pronucleophiles to the 4-position of these substrates indicated the possibility of a new reactivity pattern for alkynoates-nucleophilic addition at the α-position as shown in Scheme 1 as a new source of α-substituted alkyl acrylates.

An important point is the ability of the nucleophile to undergo simple Michael addition in preference to the α-attack since phosphines could also serve as general base catalysts for conjugate additions[1,4] Alkyl propiolates should be particularly prone to undergo such Michael additions. Although the proposed route of Scheme 1 requires both general acid and base catalysis, the nucleophilic α-addition of NH-acids such as pyrrole, indole, imidazole, or benzimidazole to alkyl propiolates was

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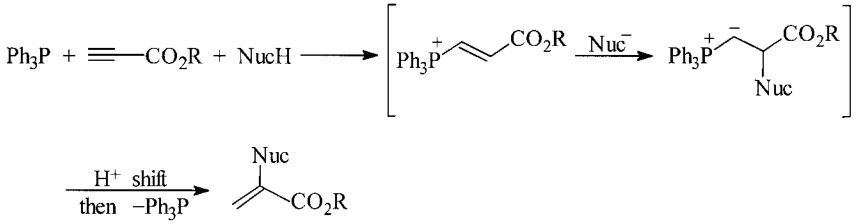
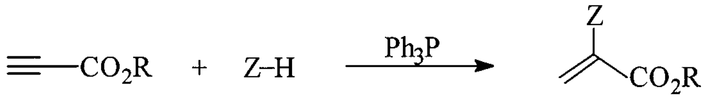
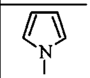
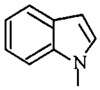
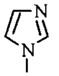
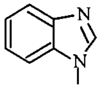


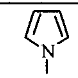
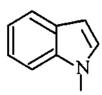
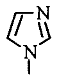
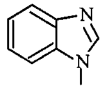
SCHEME 1

carried out under neutral conditions. Thus, methyl or ethyl propiolate undergo a smooth α-addition reaction with the NH-acids in the presence of a catalytic amount of triphenyphosphine to produce α-substituted alkyl acrylates in 80–90% yield (see Scheme 2).



1	R
a	Me
b	Et

2	Z
a	
b	
c	
d	

3	Z	R	%Yield
a		Me	80
b		Et	82
c		Me	88
d		Et	90
e		Me	88
f		Et	87
g		Me	88
h		Et	85

SCHEME 2

The structures of compounds **3a–h** were deduced from their elemental analysis and their IR, ^{1}H, and ^{13}C NMR spectra. The mass spectra of these α-substituted alkyl acrylates are fairly similar and exhibit molecular ion peaks.

The ^{1}H NMR spectra of compounds **3a–h** exhibited two slightly broad single peaks at $\delta = 5.7$–6.0 and $\delta = 6.1$–6.6 for the two diastereotopic protons of the methylene group. The alkoxy groups and the heterocyclic moieties give characteristic signals at appropriate chemical shifts (see Experimental section). Further evidence was obtained from the ^{13}C NMR spectra which displayed a methylene carbon resonance at about $\delta = 115$–123.

The structural assignments of compounds **3a–h** made on the basis of their NMR spectra are supported by their IR spectra. Of special interest are the strong carbonyl absorption bands at 1733–1728 cm^{-1} for all compounds. The characteristic =C—H out-of-plane bending absorption of the 1,1-disubstituted alkene ($RR'C{=}CH_2$) appears as an intense band at about 859-887 cm^{-1} (see Experimental section).

In summary, the reaction of NH-acids such as pyrrole, indole, imidazole, or benzimidazole with alkyl propiolates in the presence of triphenyphosphine provides a simple one-pot entry into the synthesis of α-substituted alkyl acrylates of potential synthetic interest.

EXPERIMENTAL

Alkyl propiolates were obtained from Fluka (Buchs, Switzerland). Pyrrole, indole, imidazole, and triphenylphosphine were obtained from Merck (Germany) and were used without further purification. ^1H and ^{13}C NMR spectra were measured with a BRUKER DRX-300 AVANCE spectrometer at 300 and 75 MHz respectively. Mass spectra were recorded on a Hewlett-Packard MSD 5973 mass spectrometer operating at an ionization potential of 70 eV. FT-IR spectra were recorded on a Bomem spectrometer. Elemental analyses were performed using a Heraeus CHN—O—Rapid analyzer.

The typical procedure for the preparation of 2-prrrol-l-yl-acrylic acid methyl ester (**3a**) is described as an example. To a magnetically stirred solution of 0.13 mL pyrrole (2 mmol) and 0.17 mL methyl propiolate (2 mmol) in 5 mL of dichloromethane was added dropwise a mixture of 0.52 g of triphenylphosphine (2 mmol) in 2 mL of dichloromethane at 0°C. The reaction mixture was then allowed to warm up to room temperature. After 24 h the solvent was removed under reduced pressure and the residue was purified by column chromatography. The solvent was removed and the product was obtained as a light-yellow oil, 0.24 g, 80%; IR (neat) (ν_{max}, cm^{-1}) 1733 (C=O), 1629 (C=C), 1235 and 1127 (C—O), 887 (=CH_2 bending); ^1H NMR (300 MHz, δ, $CDCl_3$): 3.89 (3 H, s, OCH_3), 5.70 (1 H, s, CH), 6.11 (1 H, s, CH), 6.28 (2 H, m, β-CH of pyrrole) and 6.93 (2 H, m, α-CH of pyrrole), ^{13}C NMR (75 MHz, δ, $CDCl_3$): 53.08 (OCH_3), 110.27 (β-CH), 116.24 (CH_2), 121.65 (α-CH), 137.65 (C), 164.07 (C=O). MS, *m/z* (%): 152 ($M^+ + 1$, 5), 147 (24), 135 (3), 121 (6), 119 (8), 81 (17), 57 (100). Analysis: Cal. for $C_8H_9NO_2$ (151.16): C, 63.56; H, 6.00; N, 9.27. Found: C, 63.7; H, 6.2; N, 9.1.

Selected Data for 2-Prrrol-1-yl-Acrylic Acid Ethyl Ester (3b)

Light-yellow oil, 0.27 g, 82%; IR (neat) (ν_{max}, cm^{-1}) 1729 (C=O), 1629 (C=C), 1234 and 1125 (C–O), 864 (=CH$_2$ bending); ^{1}H NMR (300 MHz, δ, CDCl$_3$): 1.39 (3 H, t, $^3J_{HH}$, 7.1 CH$_3$), 4.38 (2 H, q, $^3J_{HH}$ 7.1, CH$_2$), 5.69 (1 H, s, CH), 6.10 (1 H, s, CH), 6.29 (2 H, m, β-CH of pyrrole); and 6.96 (2 H, m, α-Ch of pyrrole); ^{13}C NMR (75 MHz, δ, CDCl$_3$):14.53 (CH$_3$), 62.26 (OCH$_2$), 110.21 (β-CH), 115.73 (CH$_2$), 121.64, (α-CH), 137.90 (C), 163.57 (C=O). MS, *m/z* (%): 165 (M$^+$, 18), 152 (25), 121 (18), 19 (16), 95 (44), 67 (83), 55 (100). Analysis: Cal. for $C_9H_{11}NO_2$ (165.19): C, 65.44; H, 6.71; N, 8.48. Found: C, 65.2; H, 6.6; N, 8.3.

Selected Data for 2-Indol-1-yl-Acrylic Acid Methyl Ester (3c)

Colorless oil; 0.35 g, 88%; IR (neat) (ν_{max}, cm^{-1}) 1732 (C=O), 1632 (C=C), 1216 and 1115 (C–O), 859 (=CH$_2$ bending); ^{1}H NMR (300 MHz, δ, CDCl$_3$): 3.88 (3 H, s, OCH$_3$), 5.97 (1 H, s, CH), 6.57 (1 H, s, CH), 6.66 (1 H, m, CH), 7.18–7.35 (4 H, m, CH), 7.66 (1 H, m, CH); ^{13}C NMR (75 MHz, δ, CDCl$_3$): 53.17 (OCH$_3$), 104.06, 110.98, 120.97, 121.50, 122.85 and 128.80 (CH), 121.76 (CH$_2$), 129.41, 136.35 and 136.80 (C), 164.49 (C=O). MS, *m/z* (%): 201 (M$^+$, 90), 185 (13), 142 (84), 115 (97), 83 (40), 69 (51), 55 (100). Analysis: Cal. for $C_{12}H_{11}NO_2$ (201.15): C, 71.62; H, 5.51; N, 6.96. Found: C, 71.7; H, 5.6; N, 6.9.

Selected Data for 2-Indol-1-yl-Acrylic Acid Ethyl Ester (3d)

Colorless oil; 0.39 g, 90%; IR (neat) (ν_{max}, cm^{-1}) 1728 (C=O), 1629 (C=C), 1200 and 1114 (C–O), 863 (=CH$_2$ bending); ^{1}H NMR (300 MHz, δ, CDCl$_3$):1.34 (3 H, t, $^3J_{HH}$ 7.1, CH$_3$), 4.35 (2 H, q, $^3J_{HH}$ 7.1, OCH$_2$), 5.95 (1 H, s, CH), 6.55 (1 H, S, CH), 6.64 (1 H, br d, CH), 7.15–7.36 (4 H, m, CH); 7.66 (1 H, br d, CH); ^{13}C NMR (75 MHz, δ, CDCl$_3$): 14.52 (CH$_3$), 62.35 (OCH$_2$), 103.97, 111.07, 120.90, 121.20, 122.74 and 128.85 (CH), 121.44 (CH$_2$), 129.42, 136.63 and 136.79 (C), 163.95 (C=O). MS, *m/z* (%): 215 (M$^+$, 15), 142 (13), 109 (35), 95 (65), 81 (84), 67 (81), 55 (100). Analysis: Cal. for $C_{13}H_{13}NO_2$ (215.16):C, 72.54; H, 6.09; N, 6.51. Found: C, 72.6; H, 5.9; N, 6.4.

Selected Data for 2-Imidazol-1-yl-Acrylic Acid Methyl Ester (3e)

Light-yellow oil; 0.27 g, 88%; IR (neat) (ν_{max}, cm^{-1}) 1733 (C=O), 1653 (C=C), 1221 and 1100 (C–O), 877 (=CH_2 bending); ^1H NMR (300 MHz, δ, $CDCl_3$): 3.90 (3 H, s, OCH_3), 5.86 (1 H, br s, CH), 6.30 (1 H, br s, CH), 7.12 (1 H, br s, CH), 7.15 (1 H, m, CH) and 7.76 (1 H, br s, CH); ^{13}C NMR (75 MHz, δ, $CDCl_3$): 53.45 (OCH_3), 119.63 (CH_2), 119.80, 129.95 and 137.55 (CH), 134.69 (C), 163.03 (C=O). MS, *m/z* (%): 152 (M^+, 27), 137 (14), 121 (18), 97 (56), 93 (21), 83 (67), 68 (32), 55 (100). Analysis: Cal. for $C_7H_2O_2$ (152.08): C, 55.26; H, 5.3; N, 18.41. Found: C, 55.4; H, 5.4; N, 18.3.

Selected Data for 2-Imidazol-1-yl-Acrylic Acid Ethyl Ester (3f)

Light-yellow oil; 0.29 g, 87%; IR (neat) (ν_{max}, cm^{-1}) 1728 (C=O), 1634 (C=C), 1221 and 1125 (C–O), 878 (=CH_2 bending); ^1H NMR (300 MHz, δ, $CDCl_3$):1.36 (3 H, t,$^3J_{HH}$ 7.1, CH_3), 4.33 (2 H, q, $^3J_{HH}$ 7.1 OCH_2), 5.82 (1 H, br s, CH), 6.28 (1 H, br s, CH), 7.10 (1 H, br s, CH), 7.14 (1 H, m, CH) and 7.75 (1H, br s, CH; ^{13}C NMR (75 MHz, δ, $CDCl_3$): 14.47 (CH_3), 62.73 (OCH_2), 119.24 (CH_2), 119.81, 129.85 and 137.54 (CH), 134.93 (C) and 162.52 (C=O). MS, *m/z* (%): 167 (M^++, 1, 15), 166 (M^+, 18), 152 (21), 121 (22), 95 (59), 81 (75), 69 (78). Analysis: Cal. for $C_8H_{10}N_2O_2$ (166.09):C, 57.82; H, 6.07; N, 16.86. Found: C, 57.9; H, 6.2; N, 16.7.

Selected Data for 2-Benzoimidazol-1-yl-Acrylic Acid Methyl Ester (3g)

Light-yellow oil; 0.36 g, 88%; IR (neat) (ν_{max}, cm^{-1}) 1732 (C=O), 1636 (C=C), 1271 and 1215 (C–O), 882 (=CH_2 bending); ^1H NMR (300 MHz, δ, $CDCl_3$): 3.85 (3 H, s, OCH_3), 6.04 (1 H, s, CH), 6.63 (1 H, s, CH), 7.31 (3 H, m, CH benzimidazole ring), 7.82 (1 H, m, CH benzimidazole ring) 8.04 (1 H, s, CH); ^{13}C NMR (75 MHz, δ, $CDCl_3$): 53.51 (OCH_3), 110.89, 120.89, 123.31 (CH), 123.47 (CH_2), 124.20 and 143.28 (CH), 133.52, 134.05 and 143.66 (C), 163.03 (C=O). MS, *m/z* (%): 202 (M^+, 75), 187 (8), 142 (100), 117 (10), 102 (66), 89 (35). 76 (30). Analysis: Cal. for $C_{11}H_{10}N_2O_2$ (202.14): C, 65.33; H, 4.99; N, 13.86. Found: C, 65.5; H, 5.1; N, 13.7.

Selected Data for 2-Benzoimidazol-1-yl-Acrylic Acid Ethyl Ester (3h)

Light-yellow oil; 0.37 g, 85%; IR (neat) (ν_{max}, cm^{-1}) 1728 (C=O), 1633 (C=C), 1269 and 1204 (C—O), 864 (=CH_2 bending); ^{1}H NMR (300 MHz, δ, $CDCl_3$):1.31 (3 H, t,$^3J_{HH}$ 7.1, CH_3), 4.33 (2 H, q, $^3J_{HH}$ 7.1, OCH_2), 6.04 (1 H, s, CH), 6.63 (1 H, s, CH), 7.31 (H, m, CH), 7.83 (H, m, CH) and 8.06 (1H, s, CH); δ_C 14.48 (CH_3), 62.84 (OCH_2), 110.97, 120.85 (CH), 123.02 (CH_2), 123.29, 124.14, 143.31 (CH), 133.82, 134.04, 143.61 (C) and 162.75 (C=O). MS, *m/z* (%): 217 (M^++, 1, 88), 216 (M^+, 100), 187 (6), 144 (15), 117 (6). Analysis: Cal. for $C_{12}H_{12}N_2O_2$ (216.15):C, 66.65; H, 5.59; N, 12.96. Found: C, 66.8; H, 5.7; N, 12.8.

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